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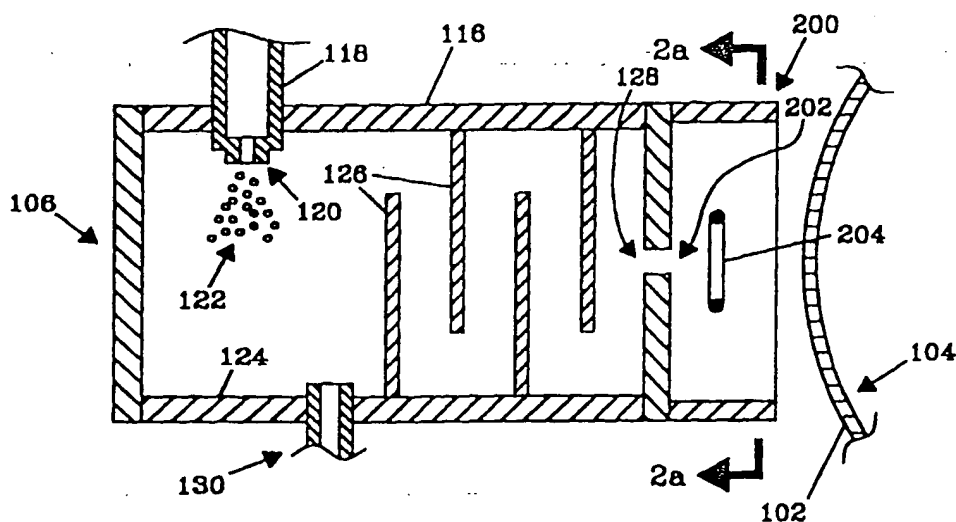
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<p>(21) International Application Number: PCT/US98/20741</p> <p>(22) International Filing Date: 29 September 1998 (29.09.98)</p> <p>(30) Priority Data: 08/939,594 29 September 1997 (29.09.97) US</p> <p>(71) Applicant: BATTELLE MEMORIAL INSTITUTE (US/US); Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).</p> <p>(72) Inventor: ALFINITO, John, D.; 2713 Kyle Road, Kennewick, WA 99338 (US).</p> <p>(74) Agent: ZIMMERMAN, Paul, W.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).</p>	<p>(81) Designated States: BR, CA, CN, JP, MX; European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	

(54) Title: PLASMA ENHANCED CHEMICAL DEPOSITION WITH LOW VAPOR PRESSURE COMPOUNDS



(57) Abstract

Generally, the apparatus of the present invention is (a) a flash evaporation housing (116) with a monomer atomizer (120) for making monomer particles (122), heated evaporation surface (124) for making an evaporate from the monomer particles, and an evaporate outlet (128), connected to (b) a glow discharge electrode (204) creating a glow discharge plasma from the evaporate, wherein (c) the substrate (104) is proximate the glow discharge plasma for receiving and cryocondensing the glow discharge plasma thereon. The method of the present invention has the steps of (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a substrate and cross-linking the glow discharge plasma thereon, wherein the cross-linking results from radicals created in the glow discharge plasma and achieves self curing.

PLASMA ENHANCED CHEMICAL DEPOSITION  
WITH LOW VAPOR PRESSURE COMPOUNDS

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FIELD OF THE INVENTION

The present invention relates generally to a method of making plasma polymerized films. More specifically, the present invention relates to making a plasma polymerized film via plasma enhanced chemical deposition with a flash evaporated feed source of a low vapor pressure compound. As used herein, the term "(meth)acrylic" is defined as "acrylic or methacrylic". As used herein, the term "cryocondense" and forms thereof refers to the physical phenomenon of a phase change from a gas phase to a liquid phase upon the gas contacting a surface having a temperature lower than a dew point of the gas.

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BACKGROUND OF THE INVENTION

The basic process of plasma enhanced chemical vapor deposition (PECVD) is described in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part IV, Chapter IV - 1 Plasma Deposition of Inorganic Compounds, Chapter IV - 2 Glow Discharge Polymerization, herein incorporated by reference. Briefly, a glow discharge plasma is generated on an electrode that may be smooth or have pointed projections. Traditionally, a gas inlet introduces high vapor pressure monomeric gases into the plasma region wherein radicals are formed so that upon subsequent collisions with the substrate, some of the radicals in the monomers chemically bond or cross link (cure) on the substrate. The high vapor pressure monomeric gases include gases of  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$ , or gases generated from high vapor pressure liquid, for example styrene (10 torr at 87.4 °F (30.8 °C)), hexane

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requires two sequential steps, cryocondensation followed by curing or cross linking, that are both spatially and temporally separate.

According to the state of the art of making plasma polymerized films, PECVD and flash evaporation or glow discharge plasma deposition and flash evaporation have not been used in combination. However, plasma treatment of a substrate using glow discharge plasma generator with inorganic compounds has been used in combination with flash evaporation under a low pressure (vacuum) atmosphere as reported in J.D. Affinito, M.E. Gross, C.A. Coronado, and P.M. Martin, "Vacuum Deposition Of Polymer Electrolytes On Flexible Substrates." Paper for Plenary talk in "Proceedings of the Ninth International Conference on Vacuum Web Coating", November 1995 ed R. Bakish, Bakish Press 1995, pg 20-36., and as shown in FIG. 1. In that system, the plasma generator 100 is used to etch the surface 102 of a moving substrate 104 in preparation to receive the monomeric gaseous output from the flash evaporation 106 that cryocondenses on the etched surface 102 and is then passed by a first curing station (not shown), for example electron beam or ultraviolet radiation, to initiate cross linking and curing. The plasma generator 100 has a housing 108 with a gas inlet 110. The gas may be oxygen, nitrogen, water or an inert gas, for example argon, or combinations thereof. Internally, an electrode 112 that is smooth or having one or more pointed projections 114 produces a glow discharge and makes a plasma with the gas which etches the surface 102. The flash evaporator 106 has a housing 116, with a monomer inlet 118 and an atomizing nozzle 120, for example an ultrasonic atomizer. Flow through the nozzle 120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas that flows

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(c) the substrate is proximate the glow discharge plasma for receiving and cryocondensing the glow discharge plasma thereon. All components are preferably within a low pressure (vacuum) chamber.

5           The method of the present invention has the steps of  
          (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate;           (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and

10           (c) cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon, wherein the crosslinking results from radicals created in the glow discharge plasma and achieves self curing.

15           It is an object of the present invention to provide an apparatus and method combining flash evaporation with glow discharge plasma deposition.

          It is an object of the present invention to provide an apparatus and method of making a self curing polymer  
20   layer.

          It is another object of the present invention to provide an apparatus and method of making a self curing PML polymer layer.

          It is another object of the present invention to  
25   provide an apparatus and method of PECVD deposition of low vapor pressure monomer.

          An advantage of the present invention is that it is insensitive to a direction of motion of the substrate because the deposited monomer layer is self curing. In  
30   the prior art, the deposited monomer layer required a radiation curing apparatus so that the motion of the substrate had to be from the place of deposition toward the radiation apparatus. Another advantage of the present invention is that multiple layers of materials  
35   may be combined. For example, as recited in U.S. patents

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120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas or evaporate that flows past a series of baffles 126 to an evaporate outlet 128 and cryocondenses on the surface 102.

Cryocondensation on the baffles 126 and other internal surfaces is prevented by heating the baffles 126 and other surfaces to a temperature in excess of a cryocondensation temperature or dew point of the evaporate. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to large surfaces 102. The evaporate outlet 128 directs gas toward a glow discharge electrode 204 creating a glow discharge plasma from the evaporate. In the embodiment shown in FIG. 2, the glow discharge electrode 204 is placed in a glow discharge housing 200 having an evaporate inlet 202 proximate the evaporate outlet 128.

In this embodiment, the glow discharge housing 200 and the glow discharge electrode 204 are maintained at a temperature above a dew point of the evaporate. The glow discharge plasma exits the glow discharge housing 200 and cryocondenses on the surface 102 of the substrate 104.

It is preferred that the substrate 104 is kept at a temperature below a dew point of the evaporate, preferably ambient temperature or cooled below ambient temperature to enhance the cryocondensation rate. In this embodiment, the substrate 104 is moving and may be non-electrically conductive, electrically conductive, or electrically biased with an impressed voltage to draw charged species from the glow discharge plasma. If the substrate 104 is electrically biased, it may even replace the electrode 204 and be, itself, the electrode which creates the glow discharge plasma from the monomer gas.

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point to allow cryocondensation of the glow discharge plasma on the part 300 and thereby coat the part 300 with the monomer condensate and self cure into a polymer layer. Sufficiently proximate may be connected to, 5 resting upon, in direct contact with, or separated by a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode 204/substrate 104 geometry, electrical voltage and frequency, and pressure in the standard way as 10 described in ELECTRICAL DISCHARGES IN GASES, F.M. Penning, Gordon and Breach Science Publishers, 1965, hereby incorporated by reference. The substrate 300 may be stationary or moving during cryocondensation. Moving 15 includes rotation and translation and may be employed for controlling the thickness and uniformity of the monomer layer cryocondensed thereon. Because the cryocondensation occurs rapidly, within milli-seconds to seconds, the part may be removed after coating and before 20 it exceeds a coating temperature limit.

In operation, either as a method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, or as a method for making self-curing polymer layers 25 (especially PML), the method of the invention has the steps of (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) 30 cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon. The crosslinking results from radicals created in the glow discharge plasma thereby permitting self curing.

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evaporator 106 through a gas inlet 130 upstream of the  
evaporate outlet 128, preferably between the heated  
surface 124 and the first baffle 126 nearest the heated  
surface 124. Additional gases may be organic or  
5 inorganic for purposes included but not limited to  
ballast, reaction and combinations thereof. Ballast  
refers to providing sufficient molecules to keep the  
plasma lit in circumstances of low evaporate flow rate.  
Reaction refers to chemical reaction to form a compound  
10 different from the evaporate. Ballast gases include but  
are not limited to group VIII of the periodic table,  
hydrogen, oxygen, nitrogen, chlorine, bromine, polyatomic  
gases including for example carbon dioxide, carbon  
monoxide, water vapor, and combinations thereof. An  
15 exemplary reaction is by addition of oxygen gas to the  
monomer evaporate hexamethyldisiloxane to obtain silicon  
dioxide.

#### Example 1

20 An experiment was conducted to demonstrate the  
present invention as shown in FIG. 2 and described above.  
Tetraethyleneglycoldiacrylate was used as the liquid  
monomer. The heated surface was set at a temperature of  
about 650 °F (343 °C). Liquid monomer was introduced to  
25 the inlet via a capillary with 0.032 inch I.D. The  
ultrasonic atomizer had a tip with 0.051 inch I.D. Rate  
of deposition of the polymer layer was 0.5 m/min for 25  
micron thick polymer layer and 100 m/min for 1 micron  
thick polymer layer. Visual inspection of the cured  
30 polymer layer did not reveal any pin holes or other flaw.

#### CLOSURE

While a preferred embodiment of the present inven-  
35 tion has been shown and described, it will be apparent to



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I claim:

1. An apparatus in a vacuum chamber for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, comprising:

(a) a flash evaporation housing with a monomer atomizer for making monomer particles, heated evaporation surface for making an evaporate from said monomer particles, and an evaporate outlet; and

(b) a glow discharge electrode downstream of the evaporate outlet creating a glow discharge plasma from the evaporate; and

(c) said substrate receiving and cryocondensing said glow discharge plasma thereon.

2. The apparatus as recited in claim 1, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage.

3. The apparatus as recited in claim 1, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate.

4. The apparatus as recited in claim 1, wherein said flash evaporation housing has opposing baffles placed between a heated surface and the evaporate outlet.

5. The apparatus as recited in claim 1, further comprising a gas inlet upstream of said evaporate outlet.

6. A method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto

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10. The method as recited in claim 9, wherein said acrylic monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate,  
5 caprolactone acrylate, and combinations thereof;

11. The method as recited in claim 6, wherein said substrate is cooled.

10 12. The method as recited in claim 6, further comprising adding an additional gas.

13. The method as recited in claim 12, wherein said additional gas is a ballast gas.

15 14. The method as recited in claim 12, wherein said gas is a reaction gas.

20 15. The method as recited in claim 14, wherein said reaction gas is oxygen gas and said evaporate includes hexamethyldisiloxane.

16. An apparatus for making self-curing polymer layers in a vacuum chamber, comprising:

25 (a) a flash evaporation housing with a monomer inlet, monomer atomizer for receiving a liquid monomer from said monomer inlet and making monomer particles, a heated evaporation surface for making an evaporate from said monomer particles, and an evaporate  
30 outlet; and

(b) a glow discharge electrode downstream of the evaporate outlet creating a glow discharge plasma from the evaporate; and

35 (c) said substrate for receiving, cryocondensing and crosslinking said glow discharge

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22. The method as recited in claim 21, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

5

23. The method as recited in claim 21, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate and said substrate is downstream of said monomer plasma, substantially not biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

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24. The method as recited in claim 21, wherein said monomer is selected from the group consisting of acrylic monomer, methacrylic monomer and combinations thereof.

20

25. The method as recited in claim 24, wherein said acrylic monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate, and combinations thereof;

25

26. The method as recited in claim 21, wherein said substrate is cooled.

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27. The method as recited in claim 21, wherein said low vapor pressure is less than about 10 torr at 83 °F (28.3 °C).

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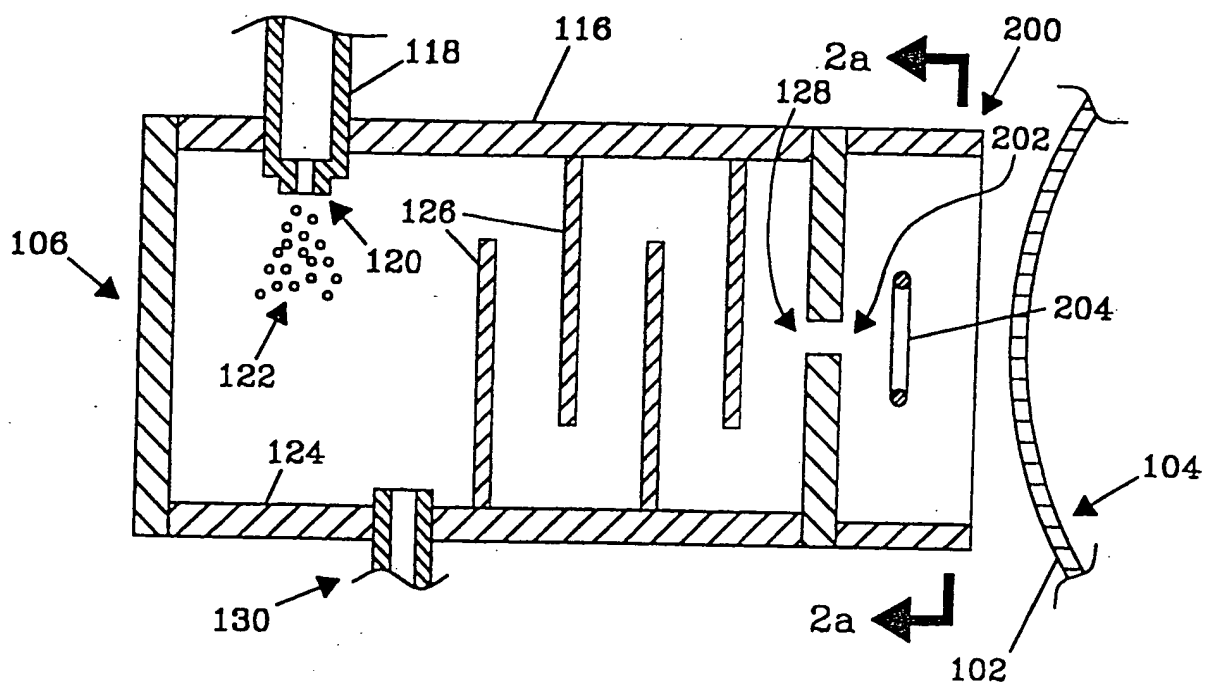


Fig. 2

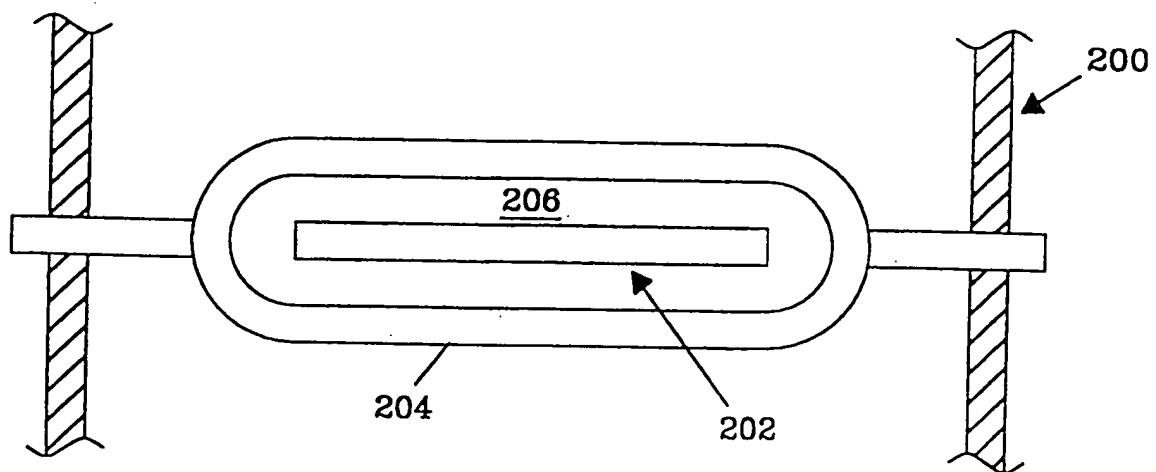


Fig. 2a

# INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/US 98/20741

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C23C16/44 C23C16/50 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C23C B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AFFINITO J D ET AL: "HIGH RATE VACUUM DEPOSITION OF POLYMER ELECTROLYTES" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 14, no. 3, PART 01, May 1996, pages 733-738, XP000620547 see the whole document	1, 16, 21
A	US 5 032 461 A (SHAW DAVID G ET AL) 16 July 1991 see column 8, line 24 - column 13, line 10; figures 2, 2A, 5	1, 16, 21
A	US 5 620 524 A (FAN CHIKO ET AL) 15 April 1997 see column 5, line 7 - line 10 see column 11, line 54 - column 13, line 20; figure 1	1, 16, 21
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

information on patent family members

Inter national Application No

PCT/US 98/20741

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5032461 A	16-07-1991	US 4842893 A	27-06-1989
		EP 0339844 A	02-11-1989
		JP 2043042 A	13-02-1990
		EP 0340935 A	08-11-1989
		JP 1316450 A	21-12-1989
		BR 8406885 A	29-10-1985
		EP 0147696 A	10-07-1985
		JP 7082961 B	06-09-1995
		JP 63072107 A	01-04-1988
		JP 7082962 B	06-09-1995
		JP 63072108 A	01-04-1988
		JP 1482591 C	27-02-1989
		JP 60153113 A	12-08-1985
		JP 63031929 B	27-06-1989
		US 5018048 A	21-05-1991
		US 5097800 A	24-03-1992
		US 5125138 A	30-06-1992
		BR 8502606 A	04-02-1986
US 5620524 A	15-04-1997	NONE	
EP 0299753 A	18-01-1989	US 4847469 A	11-07-1989
		CA 1295896 A	18-02-1992
		DE 3878328 A	25-03-1993
		JP 1085102 A	30-03-1989
		JP 1989207 C	08-11-1995
		JP 7022642 B	15-03-1995